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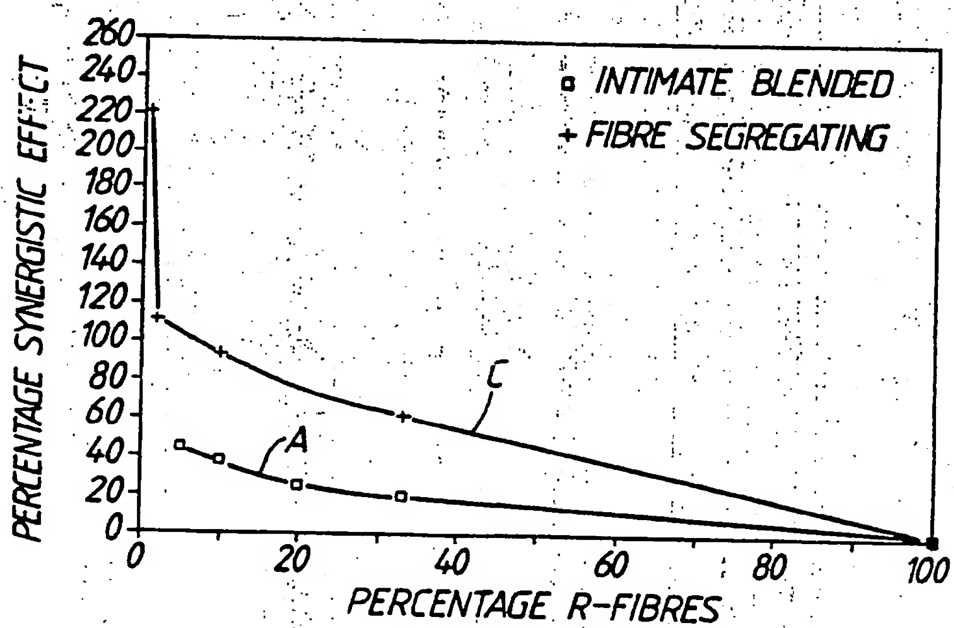

(57) Abstract

A method of forming flame resistant combination of at least two flame resistant staple fibre components, in sliver, roving, single or plied yarn, woven or knitted fabric form, and in which one of the components of the combination is kept deliberately, positively or otherwise intentionally segregated with respect to the other component or components of the combination. The combination is intended for use in making garments, articles of apparel or clothing systems incorporating predominantly or at least partially fabrics including threads with the segregated components.

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IMPROVEMENTS IN FLAME RESISTANT MATERIALS

BACKGROUND OF THE INVENTION

This invention relates to methods of producing flame resistant materials which are particularly suitable for withstanding the effects of relatively high temperatures.

It is known to use protective clothing for the purposes of protecting people who are inadvertently or otherwise exposed to conditions of extreme heat flux and very high temperature flames. A prime function of protective clothing is to protect the user from the effects of extreme heat and flames for as long as possible or, in the case of an emergency, at least as long as may be necessary, to be able to escape from the region at which extreme temperatures occur to a location at a lesser and more acceptable temperature level. In particular, any protective clothing is intended to shield the body of the user for as long as may be necessary for the enabling survival of the person being exposed to the extreme temperatures.

In the case of persons whose occupations inherently involve the possibility of being subjected to extreme heat and very high temperature flames such as for, for example, military personnel, aircraft air or ground crews, racing car drivers, police personel, fire services personnel, workmen in certain industrial activities there must always be an ongoing continuous possibility that such persons may at any instant i.e., in the event of an accident, or as a result of deliberate intention, eg., by the enemy, be subjected to extreme temperature heat and flame. In such

cases every second counts as every person in danger will try to escape but needs a certain amount of time.

At the same time it will be necessary for such persons to be able to move relatively freely for long periods without being excessively encumbered by the protective clothing. In other words, the wearability i.e., the comfort aspects of the materials forming the clothing has to be taken into consideration. In this case it will be appreciated that a protective clothing material may be formed from more than one layer of fabric of which a first layer, the outer layer, has to be able to provide the shielding or screening capability against the heat and flames, whilst a second layer serves to provide a layer of insulation which retards the penetration of heat through the clothing to the user. In this connection it will be appreciated that where the user's clothing comprises several garments the heat insulation afforded can be regarded as not only comprising the outer garments (i.e., those more conventionally regarded as protective clothing) but also the underwear of the user since this too gives a degree of heat insulation.

Depending on the application site i.e., depending on the chance of occurance of the calamities and the envoironmental aspects, different insulation compromises will have to be chosen between; that is, will have to be made. The insulation will be realised or provided by the total clothing system, normally by one or more fabric layers made of the same or different materials.

In practice, the outermost layer of a protective clothing system can be regarded as being the most important part of the protective clothing since it is this layer which has to withstand the major part of the effect of extreme heat conditions, and since this layer as

mentioned has to act as the shielding layer not only with respect to the user's body i.e., skin but also as a means of protection for the insulation providing layer or layers of the clothing.

It has been established that the fabric used for forming a shielding layer must be able to satisfy or fulfil very special conditions. First of all the material must be flame resistant. That is the material has to be able to exhibit a limiting oxygen index (L.O.I.) of at least 26.5 when in fabric form. In other words the material needs to be self extinquishing when the ignation source is removed. (This criteria has been considered by L. Bebisek in Textile Chemist & Colorist Vol 6, No 2, 1974 pages 25-29). In addition, it is necessary that when the material is exposed to an intense heat flux the material must remain as an uninterrupted surface for as long as possible.

Many proposals have been made for materials capable of providing flame resistant properties. Thus fibrous materials natural or artificial have been proposed. These fibres have included, for example, cotton, wool, viscose rayon and/or proteic, which when in a fabric form have been treated to decrease flammability.

It has been proposed to render artificial or synthetic fibres e.g., viscose rayon, polyesters, acrylics which are normally flammable inflammble by incorporating therein flame retardent additives during manufacture. It has also been proposed to produce staple fibres from polymers which are inherently flame resistant. Such staple fibres include polyvinylchloride; polyimide; polyamide-imide; polytetrafluoroethylene; polyaccrylnitril and polymetaphenyleneisophtalamide; etc.

For convenience, in this specification flame

resistant fibres in general will be called FR-Fibres.

A further group of fibres characterised by materials such as the following; polybenzimidazoles (PBI-Fibre of American Celanese); polyparaphenyleneterephthalamide (the so-called KEVLAR Fibre of Du Pont de Nemours and the TWARON Fibre of Enka BV.); formophenolic resin fibre (PHILENE fibre C.R.I.R. France; cross-linked polyacrylic acid (INIDEX of Courtaulds Ltd. UK) and certain heat treated/cyclised acrylics (carbonised fibres of Courtaulds Ltd., Sigri Electrographit GmbH, Stackpole Carbon Corporation and others) have been proposed as fibres with flame resistant properties. This group of materials will hereinafter be called R-Fibres.

In general FR-Fibres when spun into yarns and woven into fabrics have been found to deteriorate substantially or show high thermal shrinkage and rapid 'burst open' on exposure to flames and intense heat. Also in general R-Fibres have been found when in fabric form to be able to withstand intense thermal fluxes for a worthwhile time period with far less heat shrinkage and without 'burst-open' or with a delayed 'burst-open' together with retention of their flexibility accompanied by a certain amount of strength for time periods far longer than those afforded by FR-Fibres under the same conditions.

In spite of the apparent improved capability of R-Fibres as compared with FR-Fibres the R-Fibres have not achieved common acceptance for use in protective clothing since it has been found that the R-Fibres have some properties which have resulted in limiting the use of the R-Fibres for weaving protective clothing fabrics.

Some of the reluctance to use R-Fibres has been based, for example, on the adverse properties of poor

dyeability and in some instances inherent bright colouring and poor light fastness. Also some mechanical properties like the abrasion resistance are not optimal for fabrics in daily wear uses.

THE PRIOR ART

It has been proposed in United States Patent No 4,198,494 to provide an intimate blend of meltable FR-Fibres and R-Fibres for the purposes of producing a fabric for protective clothing. In the specification of this United States Patent a meltable FR/R-fibre blend including at least 15% of FR-Fibres and at least 3% of R-Fibres has been proposed. In this blend the individual fibres are not preferentially segregated within any particular region of the blend, other than that which might occur as a consequence of the normal fluctuation in fibre distribution expected on purely statistical grounds. The fabric woven from the blend has been found to provide a synergistic effect in relation to the breaking strength during a ten seconds exposure to a heat flux of $8.4 J/cm.^2 s$ (i.e., $2\ cal/cm^2s.$) and hereinafter identified as 'in flame condition'. The term 'synergistic' is used in the United States Patent in the sense that the strength when in the 'in flame condition' of a fabric formed from the blend is significantly higher than the sum of the strength contributions from the individual components of the fabric when in the 'in flame condition'.

In the United States Patent No 4,198,494 it has also been proposed to provide a modified flame test to test the FR and R fibres. (Column 2 lines 56-60 and Column 3 lines 4-31). The test has been used to investigate the extensive inter-fibre fusion and the so-called 'flame strength' as being the strength of the fabric 'in flame condition'.

It has been found that this test lacks accuracy and reproducability in measuring the flame strength. Especially if very light fabrics like the 'residue' fabrics as mentioned in Example I of the above mentioned United States Patent (Column 3 lines 56-58) are tested. The sudden heat flux of 2 cal/sq.cm. ($8.4 J/cm.^2 s$) by means of a Meker burner is too sudden and too intense and the power of the flame deteriorates the measurement.

OBJECT OF THE INVENTION

It is an object of the present invention to provide an improved flame resistant material.

STATEMENTS OF THE INVENTION

Broadly, according to an aspect of the present invention there is provided a method of forming a flame resistant combination of at least two staple fibre components, in a sliver, roving, single or plied yarn or woven or knitted fabric form, and characterised by the step of keeping one of the components deliberately, positively or otherwise intentionally segregated with respect to the remaining component or components of the combination.

In accordance with a further aspect of the invention there is provided a method of forming a flame resistant combination of at least two flame resistant staple fibre components in woven or knitted fabric form, and characterised in that one of the components is deliberately, positively or otherwise intentionally segregated with respect to the remaining component or components of the combination in such manner that the 'heat performance' properties, as hereinafter defined, are

synergistically related with respect to the corresponding properties of the individual components.

Preferably, the components are assembled in such manner that said combination when in woven fabric form includes in the warp and weft directions of the fabric flame resistant yarns which comprise said one component, said flame resistant yarns being spaced apart by a distance having a maximum value of 20 times the thickness of the fabric.

In accordance with a still further proposal of the invention there is provided a flame resistant fabric including threads incorporating a flame resistant combination of at least two staple fibre components, in single or plied yarn form of which at least some of the thread forming yarns are characterised by having at least one of the components thereof deliberately, positively or otherwise intentionally segregated with respect to the remaining component or components of the combination.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention Reference will now be made to the accompanying drawings in which:-

Figure 1 is a very schematic oblique representation of apparatus for carrying out a proposed test for assessing the properties of heat resistant materials particularly those produced by the proposals of the invention;

Figure 2, is a schematic side view of the apparatus of Figure 1;

Figures 3 and 4 are graphs representing inter-relationships of defined factors of materials of the invention and prior art.

DESCRIPTION OF THE PREFERRED METHODS AND ARRANGEMENTS OF THE INVENTION

Referring to figures 1 and 2 which are concerned with the apparatus involved in an accurate test which is proposed for assessing the properties of the heat resistant materials. The test has been developed since in relation to the disclosure of the United States Patent it is questionable whether the measurement of the 'flame strength' is a measure of the 'heat performance' of the fabric to perform as a shielding layer. The term 'heat performance' will be considered in detail hereinafter.

From a realistic point of view in regard to people who are still able, to escape from said region at which extreme temperatures occur it is proposed to lower the

heat flux to half of the lower limit of a fuel oil conflagration temperature range (3.2 J/cm.^{2} s) In this proposal in place of the convective heat of a Meker burner (not shown) the radiant heat of a quartz infrared tube 1 of 500 Watts is used. The current supplied to this quartz tube can be changed by a transformer (not shown) to obtain a heat flux of 3.2J/cm^{2}s. As can be seen from the accompanying drawing Figure 1 a test fabric strip 2 of 20 millimetres wide is suspended from a metal strip 3 positioned above the quartz tube 1 by means schematically indicated at 4 and is held out of the region of the tube 1 until the test commences. The fabric strip 2 supports at its lower end 6 by way of an attachment means 7 a reference weight 8 which in the proposals under consideration weighs 20 grammes. The means 7 can be engaged by the means 5 to hold the fabric away from the tube 1. As will be noted from the figures 1 and 2 the fabric strip 2 wraps around a portion only of the tube. In practice, it is required that the chordal length 9 of the wrap, which latter is the length of contact between the fabric and the tube, should be 7 millimetres. This is indicated in Figure 2.

In the United States Patent the 'flame strength' is measured by applying a fixed flame-time of ten seconds and by having the fabric strips support different weights. (Column 3 lines 21-27). It is proposed by using the quartz tube 1 and the fixed weight 8 to measure the time that the fabric has to be subjected to the heat flux before the fabric can no longer support the fixed weight.(e.g., it will be understood that the time required is effectively a characteristic of the amount of heat flux in Joules)

Hence the means (aperture) 5 which shields and holds the fabric strip out of the quartz tube region can be retracted. The fabric strip 2 will swing against the quartz tube and an area of 1.4 square centimetres will be in contact with the quartz tube 1 this being the area related to the above mentioned chordal length 9. As a result the fabric strip 2 will be exposed to a heat flux of 4.5 J/s. A timer is arranged to measure the time required for the weight 8, supported by the fabric strip 2 to fall down.

By using the proposed Heat Performance Test the amount of heat flux that the fabric can withstand, can be calculated as being the 'heat performance' of the fabric.

This amount of heat flux in Joules can be divided by the total tex (denier) of all of the yarns running in the vertical (test) direction in order to compute the 'heat performance' in milliJoules (mJ) per decitex (dtex) of the test fabric.

As mentioned above the proposed Heat Performance Test measures time. The time which is so important while escaping the effects of extreme heat and flame. As every second is important in terms of distance a person can move from the heat and flame location each second and each additional second increases the possibility of survival.

To determine whether a fibre qualifies as a R-fibre component in accordance with this invention, a fabric formed from the fibre may be subjected to the above mentioned test. If the 'heat performance' per decitex is at least 15mJ the fibre can be considered to be a R-fibre.

In an investigation of the synergistic property

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mentioned in the above mentioned United States Patent (column 5 line 61 until column 6 line 4 the following test fabrics were made.

Different intimate blends of FR and R-fibres were prepared.

The FR component is meta-aramide (polymetaphenyleisophtahalamide) fibre of 40 millimetre (1.6 inches) fibre length and 1.7 decitex (1.5 dpf) fibre fineness. (APYEIL of UNITIKA Ltd. Japan).

The R-fibre component is para-aramide (polyparaphenyleneterephtalamide) fibre made by Du PONT, U.S.A. and sold under the trade name 'KEVLAR'. The fibre length is 38 millimetre (1.5 inches) and the fibre fineness is 1.7 decitex (1.5 dpf). Different amounts of these fibres are mixed in fibre form and spun into single yarns of 49 tex (12 c.c.). The yarns are woven into plain weave fabrics of approximately 21 x 21 threads per centimetre after removing sizing components and dirt (desizing). The basis weights of these fabrics have ranges of 227-241 grammes/square metre (6.7-7.1 oz/square yard).

The 'heat performance' of these fabrics were measured and are as shown in Table 1. The intimate blended data of Table 1 is presented as Graph A of Figure 3.

TABLE 1

COMPOSITION (%FR/%R	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT compared with 100% R-fibre
100/0	0.9	neg.
95/5	24.6	45%
90/10	23.5	38%
80/20	21.3	25%
67/33	20.5	20%
0/100	17.0	0%

It is important to note the differences of these figures with the flame strength measurements mentioned in the United States Patent. In accordance with the United States Patent's 'flame strength' figures the fabric of 100% para-amide (KEVLAR) has a much higher 'heat performance' than the fabric of 100% meta-aramide. I.e., 17.0 mJ/dtex compared with 0.9mJ/dtex.

For a better understanding of the data of table 1 it should be noted that, in practice, in terms of escaping times these figures (for these fabrics) represents 78 seconds breaking time and four seconds breaking time. The figures also show the synergistic interaction between the fibres in the intimate blend.

This is completely unexpected and contrasts with the flame strength figures of the United States Patent.

The synergistic effect, as used in the sense of the

present invention, can be seen from Table 1 as the relation of the 'heat performance' of the intimate blended fabrics compared with 'the heat performance' of the fabric of 100% R-fibres, i.e., the fabric made out of 100% of the best of the two components. The 'heat performance' of all of the fabrics of intimate blended fibres are higher than that of the 100% para-aramide fabric. It can be seen that the synergistic effect increases with a decreasing amount of para-aramide.

The accurate 'Heat Performance Test' that has been developed in relation to the present invention shows also the correctness of teaching relating to the 3-20% blend level range provided in the United States Patent claims (column 8 line 58). The increase in synergistic effect, if more than 20% para-aramide is blended with the meta-aramide is shown to be far less as compared with the synergistic increase obtainable with blend levels less than 20%. This is shown in the lower line A of Figure 3.

The 20% blend level mentioned in the United States Patent has, as stated in column 4 lines 63-68, been chosen purely on practical grounds of non-dyeability, inherently highly coloured, poor abrasion etc. As has been shown now the 20% level is an important limit of the effective influence of the fibre component.

As mentioned in column 4 lines 56-59 of the United States Patent the lower limit of 3% R-fibre component has been chosen as to be a practical minimum level for intimate blends to ensure uniform distribution of the R-fibre component throughout the blends. The effectiveness of blend levels less than 3% will be referred to hereinafter.

According to the invention it has been found that by positively, deliberately or otherwise intentionally segregating the R-fibres involved in a flame resistant combination of flame resistant fibres an unexpected increase of the synergistic effect occurs which cannot not be explained by the gluing effect of the meltable FR-fibres as mentioned in the United States Patent (column 5 lines 1-3). The necessity of the occurance of fibres showing a gluing efffect will also be referred to hereinafter.

In order to effect a comparision between the teaching of the United States Patent and that of the present invention a yarn of 49 tex (12c.c.) of 90% meta-aramide (APYEIL) and 10% para-aramide (KEVLAR) was spun on a DREF friction-spinning machine in which all of the 10% KEVLAR para-aramide fibres were deliberately segregated in fibre form in the core of the yarn.

The yarn has been woven in a plain weave to provide a piece of fabric of 21x21 threads per centimetre comparable with the 90/10 fabric of intimate blended yarns mentioned in Table 1.

The comparison of 'heat performance' per dtex figure for the fabric of the present invention with the 'heat performance' figure of fabric of the United States Patent is shown in Table 2.

For convenience hereinafter, in this specification, intimate blended yarns will be called I-yarns and the segregated yarns of the present Application will be called S-yarns.

TABLE 2

BLEND METHOD (10%R)	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT compared with 100% R-fibre
Intimate (I)	23.5	38%
Segregated (S)	32.7	92%

As has been shown in Table 1 the 'heat performance' of the fabric of the I-yarns with a 10% R-fibre shows a synergisitc effect of 38% compared with a 'heat performance' of 17mJ/dtex of 100% R-fibre. If the R-fibres are positively, deliberately or otherwise intentionally segregated in the core of the S-yarn a synergistic effect of 92% is found which is about two and one half times more than that of I-yarn.

It will be appreciated that the proposals of the present invention are not restricted to combinations of only two staple fibre combinations but comprehends multi-component combinations as well, e.g., employing multiple FR and R components to attain the required total percentages of each type.

On a DREF friction spinning machine a yarn of 49 tex (12 c.c) yarn count is spun incorporating 63% APYEIL meta-aramide (FR) fibres of UNITIKA, JAPAN; 27% flame retardent viscose non-meltable FR-fibres of LENZING AG, AUSTRIA, and segregated in the core of the yarn 10% KEVLAR para-aramide (R) fibres of Du PONT, U.S.A. The yarns are again woven into a plain weave fabric of 21x21 threads per centimetre (thr/cm) after desizing

The heat performance is measured and amounts to 40.5

mJ/dtex which compared with the yarns with 10% R-fibre of table 2 shows a more improved synergistic effect, see Table 2A.

TABLE 2A

YARN TYPE	%R-FIBRES	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT
Ringspun	100%	17.0	0%
Intimate blended	10%	23.5	38%
Segregated	10%	32.7	92%
Segregated + 27% viscose fr	10%	40.5	138%

Another method to segregate the R-fibres in the core of a yarn is to pre-spin a very fine spun yarn of R-fibres only or to use a filament yarn of R-fibres. By using known core-spinning techniques the R-fibre pre-spun or filament yarn can be segregated in the core of the yarn.

The pre-spinning can be done with any spinning machine capable of spinning very fine yarns. The core spinning can be done by known core-spinning techniques, i.e., ring; open-end; friction-spinning machines etc. A very fine spun yarn of 100% KEVLAR para-aramide (R-fibres) has been pre-spun into a yarn count of 12 tex (50.c.c.)

On a DREF friction spinning machine the above mentioned yarn has been incorporated into the core of a yarn of APYEIL meta-aramide (FR) fibres resulting in a yarn count of 49 tex (12 c.c.) of which 24% are R-fibres. The yarns have been woven again into a 21x21 (thr/cm) fabric of a plain weave, washed and tested.

The 'heat performance' of this fabric amounts to 22.5 mJ/dtex which equals an synergistic effect of 32%.

As has been shown in Table 1 the synergistic effect of an intimate blend of 20% R-fibres amounts to 25% and decreases if the amount of R-fibre is increased. So an intimate blend of 24% R-fibre (I-yarn) shall have a synergistic effect which is less than 25%. The Ş-yarn with 24% R-fibre has a synergistic effect of 32% which is much higher and again proves the increased synergistic effect of segregated incorporation of R-fibres.

As is shown in Table 1 the synergistic effect increases when the amount of R-fibres in the fabric decreases. The decreasing of the amount of R-fibres is achieved by decreasing the amount of R-fibres in the yarns.

Another way of decreasing the amount of R-fibres in the fabric is the usage of different yarns with a different amount of R-fibres. A fabric can be made of the above mentioned S-yarn of 24% R-fibres in combination with a yarn of 0% R-fibres and the yarns can be used one after the other. In other words if one out of two yarns in the fabric contains 24% R-fibres the aggregate amount of R-fibres in the fabric is 12%.

Hence the segregation of the R-fibres can not only be exercised in the yarn but can also be exercised during

the weaving of the fabric. This is a feature of the proposals of the present invention.

Using the above mentioned S-yarn (S) containing 24% R-fibres in combination with a yarn (FR), also spun on the DREF friction-spinning machine, containing 0% R-fibres the following fabrics of 49 x 49 tex and 21 x 21 (thr/cm) are made and tested after desizing to evaluate the 'heat performances'. This is shown in Table 3 and Graph B of Figure 4.

TABLE 3

YARN USED	%R-FIBRES IN FABRIC	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT %
ALL FR-YARNS	0.0	1.3	neg
1 S+4 FR-YARNS	4.8	37.0	118
1 S+2 FR-YARNS	8.0	30.7	80
ALL S-YARNS	24..0	22.5	32

As can be seen the heat performance of the fabrics again increases when the amount of R-fibres in the fabric decreases although the amount of R-fibres in the particular S-yarn, containing the R-fibres, stays the same (24%).

Thus the increased synergistic effect obtained by deliberately segregating the R-fibres in the yarn instead of blending them intimately can also be obtained by segregating R-fibre containing yarns in the fabric.

The fabric thicknesses of the fabrics mentioned in Table 3 range between 0.51 and 0.52 millimetres. In the fabric of'1 S+4 FR yarns' the distance between two S-yarns is 2.38 millimetres. Thus the S-yarn spacing distance

can be defined as the ratio of 4.6 times the fabric thickness. If this distance is increased the danger of a small piece of fabric, bordered by the S-yarns in the warp and weft direction, breaking open will also increase. Hence, depending upon the 'heat performance' and other properties of the other component or components, the distance between two R-fibre containing yarns is limited and is not allowed to exceed 20 times the fabric thickness.

Thus, in accordance with a further aspect of the invention there is provided a flame resistant fabric of which the warp yarns and the weft yarns include in the warp and weft direction of the fabric flame resistant yarns spaced apart by a distance having a maximum value of 20 times the thickness of the fabric, said flame resistant yarns comprising R-fibres or incorporating R-fibres, said R-fibres having been deliberately, positively or otherwise intentionally preferentially segregated within the associated yarn component.

As is known single yarns can be plied or twinned. To incorporate the R-fibres deliberately segregated in the yarn, two or more yarns can be plied, of which at least one yarn (which will be only a very fine yarn compared with the other yarn components with which it is to be plied) comprises R-fibres.

As an example, the above mentioned 100% KEVLAR para-aramide (R-fibre) yarn of yarn count 12 tex (50 c.c.) can be plied with a 100% APYEIL meta-aramide (FR-fibre) of yarn count 37 tex (16 c.c.) resulting in a plied yarn combination of yarn count 49 tex (12 c.c.) in which again the amount of deliberately segregated R-fibres is 24%.

Also yarns of FR-fibres can be plied with at least one yarn of a combination of FR and R-fibres in which the

R-fibres are deliberately segregated. This is preferred to decreasing the amount of R-fibres and avoids the pre-spinning of very fine yarns of R-fibres.

Thus, in accordance with a further aspect of the invention there is provided a flame resistant combination in a ply-yarn form of at least two flame resistant staple fibre components of which one of the components is deliberately, positively or otherwise intentionally segregated and of which at least one ply comprises the R-fibre or a combination of FR and R-fibres in which the R-fibres are deliberately segregated.

The (S) yarn containing 24% R-fibres mentioned above is a yarn containing the R-fibres in (pre-spun) yarn form. As is shown above the 'heat performance' increases depending on a decreasing of the amount of R-fibres. If the pre-spinning system is used the low percentage of R-fibres can only be achieved for rather coarse yarns (thick yarns) because there are limits to the fineness of the pre-spun yarn.

The segregation of the R-fibres can also be achieved in fibre-form as in the S-yarn Example of Table 2, and thus not in a pre-spun form. As mentioned above a 10% segregated R-fibre containing S-yarn has been spun on a DREF friction spinning machine. In that case the R-fibres are not pre-spun but incorporated in the yarn in fibre form. The fibre input into the drafting part of the machine has been a sliver of FR-fibres and a roving of R-fibres. In the drafting zone the fibre-input, i.e., the sliver and the roving, will be drafted but will keep their relative placement. They will not be mixed or blended. Consequently, the R-fibre roving will be drafted only into a finer fibre bundle and will be kept segregated. This system will be called the sliver/roving

pairing system and forms a further aspect of the proposals of the invention.

Also for the (most common) ring spinning system this sliver/roving pairing system can be used to obtain the segregated R-fibres in the ring spun yarn.

By using a sliver/roving pairing system as the input for the roving frame, a roving yarn with segregated R-fibres is obtained which, after spinning on the ring spinning frame, will result in a ring spun yarn with segregated R-fibres.

As is known in the ring spinning technique the last machine in the total process where a blending of mixing of fibres occurs, are the draw frames.

By repeatedly combining six or more slivers and drawing them again into one sliver a mixing or blending of the fibres occurs. In Example 1 of the United States Patent the intimate blending was achieved on these machines (column 5 line 30).

If the sliver/roving pairing system is used on the last draw frame no blending or mixing will occur if one R-fibre roving is fed (in the middle of the other slivers fed) into the machine. Thus, the output of this last drawing frame and the input of the next machine, the roving frame, will be a sliver with segregated R-fibres. After spinning the roving on a ring spinning frame, a ring spun yarn is achieved incorporating segregated R-fibres.

Hence, in accordance with a further aspect of the invention there is provided a process for incorporating segregated R-fibres in a yarn of flame resistant fibres by means of a sliver/roving pairing system.

If the sliver/roving system is used on the last draw frame as mentioned above, the amount of R-fibres can be very small as the feeding of the machine is six or more slivers of FR-fibres and one roving of R-fibres. A percentage of 2 or, if a twistless roving, as explained hereinafter, is used even less than one percent can be achieved.

If the sliver/roving pairing system has to be used on a machine of which the input is a single sliver only, i.e., a roving frame, a DREF friction spinning machine etc., the lower limit of the percentage R-fibre cannot be too low as there are practical limits to the fineness of the roving.

Thus it is a further feature of the invention to provide a particular sliver/roving pairing system of which the roving part comprises a twistless fibre bundle made according to a twistless spinning system.

References to the twistless spinning system are made in Dutch Patent No 143,002:- Method to produce a yarn and yarns made according to the method. (also British Patent No 1,186,233; United States Patent 3,447,310; and Japenese Patent No 805,398); and also in British Patent No 1,419,108:- Process for bonding staple fibres into an essentially non-twisted yarn.

Essentially these systems consist of processes of drawing a sliver into a finer fibre bundle and, instead of twisting to strengthen the bundle, gluing the fibres together with a water soluble glue.

The twistless 'yarn' spun according to these systems can be used as a roving in the sliver/roving pairing

systems if the amount of glue used in these systems is decreased to such an amount that the drafting of the fibre bundle in the drafting zone is not afffected.

On statistical grounds it is known that in intimate blends of fibres to secure the probability of the occurance of a R-fibre, i.e., the uniform distribution of the R-fibres, the blend level has a possible practical lower limit which is said to be 3%, but which in practice has an actual limit of 5% This possible practical limit is also mentioned in the United States Patent (column 4 lines 56-59). Because of the deliberate segregation in accordance with the present invention (so not an intimate blend) the limit for combining two or more fibre components, to secure the probability of the occurance of a R-fibre, is lower than 3% and can, depending on the fibre fineness and yarn count, even be lower than 0.5%.

Using the APYEIL meta-aramide of UNITIKA as an FR-fibre and the para-aramide KEVLAR of Du PONT as a R-fibre, a 49 tex (12 c.c.) single ringspun yarn is made and woven into a plain woven fabric of 21 x 21 yarns per cm. The sliver/roving pairing system on the last draw frame is used to obtain yarns containing 1,2, 10 and 33% segregated R-fibres. After desizing the 'heat performance' is measured and the synergistic effect computed.

TABLE 4

YARN TYPE	%R-FIBRES (PARA-ARIMIDE)	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT
100% meta-aramide	0%	1.3	neg
Meta/para-aramide	1%	54.6	221%
Meta/para-aranide	2%	36.1	112%

Meta/para-aramide	10%	33.0	94%
Meta/para-aramide	33%	27.5	62%
100%para-aramide	100%	17.0	0%.

Note the meta/para-aramide mentioned in the Table 4 are S-yarns.

The increased synergistic effect due to the low percentage (1 and 2%) of R-fibres of which the probability of occurance is secured by segregation is evident. The figures of Table 4 are shown at Graph C of Figure 3.

Although modacrylic fibres show a L.O.I. value greater than 26.5, and thus will not continue to burn when the ignation source is removed, the protective effect as a shielding or screening outer layer in flame protective clothing is rather low as the fabric deteriorates rather rapidly.

A S-yarn according to the present invention is prepared from 98% modacrylic fibres of 40 millimetres (1.6 inch) fibrelength and 1.7 dtex (1.5dpf) (VELICREN FRS modacrylic fibres of SNIA SA, Italy) and deliberately segregated in the core of the yarn 2% para-aramide R-fibres (polyparaphenyleneteraphtalamide) of 40 millimetre (1.6 inches) fibrelength and 2.2 dtex (2.0 dpf) (TWARON Fibre of ENKA, The Netherlands). The spinning of the yarns was effected upon a DREF friction spinning machine using the sliver/roving pairing system and using a sliver and a twistless roving as mentioned above. The yarns of 49 tex (12 c.c.) yarn count are woven into a plain fabric of 21 x 21 (thr/cm). The same fabric of 100% VELICREN FRS Fibres and a fabric of 100% TWARON fibres is also prepared.

The 'heat performance' figures are measured and the synergistic effect calculated as shown in Table 5.

TABLE 5

YARN TYPE	%R-FIBRES	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT
100% para-aramide	100%	21.8	0%
100% modacrylic	0%	0.2	neg
98% modacrylic	2%	25.2	15%

Although the synergistic effect in relation to the 100% para aramide fabric is less striking as compared with the examples mentioned above with meta aramides the 'heat performance' of the fabric made out of modacrylic S-yarns with only 2% R-fibres according to the present invention is higher than the 'heat performance' of 100% R-fibre. The heat performance of the 98/2% S-yarn of modacrylic even equals the 95/5% I-yarn of meta-aramide of Table 1.

As mentioned earlier the increased 'heat performance' of the low percentages of R-fibres cannot be explained according to the gluing theory of the A-fibres (equivalent to organic synthetic FR-fibres of the present invention) as mentioned in The United States Patent (column 5 lines 1-3). The necessary occurance of meltable organic FR-fibres is investigated by preparing fabrics without meltable FR-fibres, but with non-organic FR-fibres only in combination with R-fibres.

On a DREF friction spinning machine the following yarns are made in 49 tex (12 c.c.)

FR-yarn 100% viscose fr (LENZING AG, AUSTRIA)
S10-YARN 90% viscose fr and 10% KEVLAR (R-fibre)

S2-YARN 98% viscose fr and 2% KEVLAR (R-fibre)

These yarns were each woven again into a fabric of 21 x 21 (thr/cm) after desizing. The heat performances have been tested showing the following figures as shown in Table 6

TABLE 6

YARN TYPE	%R-FIBRES	HEAT PERFORMANCE (mJ/dtex)	SYNERGISTIC EFFECT %
Ringspun	100	17.0	0
FR-Yarn	0	4.5	neg
S10-yarn	10	88.6	421%
S2-yarn	2	13.1	neg

As can be seen the 2% deliberately segregated R-fibres in combination with a non-organic FR-fibre is too low to achieve a sufficiently improved synergistic effect as compared with the 'heat performance' of 100% R-fibre, even though the improvement of the 'heat performance' from 4.5 mJ/dtex to 13.1 mJ/dtex shows a synergistic effect as compared with the sum of the 'heat performance' contributions from the individual components (4.6 mJ/dtex).

If 10% R-fibre is used the highly improved synergistic effect is evident. Thus since it is found possible to achieve an improved synergistic effect the occurance of meltable organic FR-fibres is not necessary.

Preferably, in accordance with a feature of the invention, the percentage weight of the deliberately, positively or otherwise intentionally segregated R-fibres, if used in combination with non-organic FR-fibres only,

should not be lower than 3%.

As mentioned earlier an important disadvantage of many proposals for flame protective materials are the high thermal shrinkage and the rapid burst-open. In the above mentioned United States Patent a 'fabric break open test' is proposed. (column 3 line 59 until column 4 line 50). This test, often nowadays called the thermal protection performance (TPP) test, has been applied on the fabrics made according to this invention exposing the fabrics to the heat flux of 8.4 mJ/cm^2s for the standardised ten seconds. The time until break-open is measured or if no break-open occured after ten seconds, it is noted as above 10 secs.

Table 7 shows the break open tests of the imtimate blended fabrics mentioned in Table 1.

TABLE 7

COMPOSITION (%FR/%r)	T.P.P. TEST (Break-Open)
100/0	3S
95/5	above 10S
90/10	above 10S
80/20	above 10S
67/33	above 10S
0/100	above 10S

The fabric made according to this patent with 10% segregated R-fibres as mentioned in Table 2 also shows a break-open of longer than 10 seconds. (above 10s).

TABLE 8

YARNS USED	%r-FIBRES IN FABRIC	T.P.P. TEST (BREAK-OPEN)
ALL FR-yarns	0.0	4s
1S+4FR yarns	4.8	above 10s (some flames)
1S+2FR yarns	8.0	above 10s
All s-yarns	24.0	above 10s

In the fabric of 4.8% R-fibres some flames were observed at the top of the fabric sample, but no break out occured.

Even the meta-aramide fabrics of S-yarns with only 1 and 2% segregated R-fibres as mentioned in table 4 and the modacrylic fabric with only 2% R-fibres as mentioned in Table 5 do not break open within 10 seconds.

The break open property of the Viscose FR fabric incorporating 2% and 10% segregated R-fibres as mentioned in Table 6 is shown as follows in Table 9

TABLE 9

YARNS USED	%R FIBRES IN FABRIC	T.P.P. TEST (BREAK-OPEN)
FR-yarn	0	1s
S10-yarn	10	above 10s
S2-yarn	2	above 10s

Examples of the 'Heat Performance' of Fabrics. All fabrics comprise 49 x 49 tex yarns (12 x 12 c.c.) and

approximately 21 x 21 thr/cm (53x53 thr/inch)

Materials	R-fibres %	I/S Yarns	Heat Performance (mJ/dtex)
Meta-aramide CONEX (Japan)	0	-	1.1
Meta-aramide APYEIL(JAPAN)	0	-	0.9
80/20% APYEIL/ Viscose fr	0	I	1.7
99% Meta-armide APYEIL	1	S	54.6
Polyimide P84 (Austria)	0	-	0.6
50%/50% P84/ Viscose fr	0	I	0.4
96% Polyimide P84	4	S	31.8
70/20% APYEIL/ Viscose fr	10	S	32.9
90% Viscose fr	10	S	88.6

CLAIMS

1. A method of forming a flame resistant combination of at least two flame resistant staple fibre components, in sliver, roving, single or plied yarn, woven or knitted fabric form, and characterised by keeping one of the components deliberately, positively or otherwise intentionally segregated with respect to the other component or components of the combination.

2. A method of forming a flame resistant combination of at least two flame resistant staple fibre components as claimed in claim 1, in a woven or knitted fabric form, and characterised in that the 'heat performance' properties, as hereinbefore defined, are synergistically related with respect to the corresponding properties of the individual components.

3. A method of forming a flame resistant combination as claimed in claim 1, and characterised by assembling the components in such manner that said one component is in a roving form and the other component or components is/are in sliver form.

4. A method of forming a flame resistant combination as claimed in claim 3, and characterised in that the roving component is twistless.

5. A method of forming a flame resistant combination as claimed in claim 1,3, or 4, and characterised by assembling the components in such manner that said combination in yarn form includes said one component concentrated in the core of the yarn.

6. A method of forming a flame resistant combination as claimed in claim 1, and characterised by assembling the components in such manner that said combination in ply-yarn form includes at least one ply comprising said one component.

7. A method of forming a flame resistant combination as claimed in claim 1, and characterised by assembling the components in such manner that said combination in ply-yarn form includes at least one ply made according to claims 3,4 or 5.

8. A method of forming a flame resistant combination as claimed in claim 2, and characterised by assembling the components in such manner that said combination in woven fabric form includes in the warp and weft directions of the fabric flame resistant yarns which comprise said one component, said flame resistant yarns being spaced apart by a distance having a maximum value of 20 times the thickness of the fabric.

9. A method of forming a flame resistant combination as claimed in claim 2, and characterised by assembling the components in such manner that said combination in woven fabric form includes in the warp and weft directions of the fabric flame resistant yarns which comprise a combination of at least two components which are assembled according to any of claims 3 to 7, said flame resistant yarns being spaced apart by a distance having a maximum value of 20 times the thickness of the fabric.

10. A method of forming a flame resistant combination as claimed in any one of claims 1 to 9, and characterised in that said one component exhibits a 'heat performance' as hereinbefore defined, having a maximum of 15mJ/dtex.

11. A method of forming a flame resistant combination as claimed in any one of claims 1 to 10, and characterised in that said one component comprises polyparaphenyleneterephtalamide and/or formophenolic and/or polybenzimidazoles and/or carbon fibres.

12. A method of forming a flame resistant combination as claimed in any of claims 1 to 11, and characterised in that said other component or components comprise(s) natural and/or artificial materials which are flame retardant treated.

13. A method of forming a flame retardant combination as claimed in claim 12, and characterised in that said other component or components comprise(s) wool and/ cotton and/or viscose rayon and/or proteic staple fibres.

14. A method of forming a flame resistant combination as claimed in any of claims 1 to 13, and characterised in that said other component or components comprise(s) artificial materials which incorporate flame retardant additives.

15. A method of forming a flame resistant combination as claimed in claim 14, and characterised in that said other component or components comprise(s) viscose rayon and/or diacetate and/or triacetate and/or proteic staple fibres.

16. A method of forming a flame resistant combination as claimed in any one of claims 1,2,3 and 5 to 15, and characterised in that said other component or components comprise(s) synthetic/organic materials which incorporate flame retardant additives.

17. A method of forming a flame resistant combination as claimed in any of claims 1 to 15, and characterised in that said other component or components comprise(s) synthetic/organic materials which incorporate flame retardant additives.

18. A method of forming a flame resistant combination as claimed in claim 16 or 17, and characterised in that said other component or components comprise(s) polyesters and/or polyamides and/or polyaccrylnitril staple fibres.

19. A method of forming a flame resistant combination as claimed in any of claims 1,2,3, and 5 to 16 and 18, and characterised in that said other component or components comprise(s) inherently flame resistant materials.

20. A method of forming a flame resistant combination as claimed in any of claims 1 to 18, and characterised in that said other component or components comprise(s) inherently flame resistant materials.

21. A method of forming a flame resistant combination as claimed in claim 19 or 20, and characterised in that said other component or components comprise(s) modacrylic and/or polyvinylchloride and/or polyimide and/or polyamide-imide and/or polytetrafluoroethylene and/or polymetaphenyleneisophtalamide and/or cross-linked polyacrylic acid.

22. A method of forming a flame resistant combination as claimed in any of claims 12 or 15, and characterised in that said one component provides between 2 to 40% by weight of the total weight of the combination.

23. A method of forming a flame resistant combination as claimed in any of claims 16,18,19 or 21, and characterised in that said one component provides between 0.5 to 40% by weight of the total weight of the combination.

24. A method of forming a flame resistant combination as claimed in any of claims 17,18,20 or 21, and characterised in that said one component provides between 0.15 to 5% by weight of the total weight of the combination.

25. A flame resistant yarn characterised by being manufactured according to the method as claimed in any of claims 5 to 7 and 10 to 24.

26. A flame resistant fabric characterised by being produced by the method as claimed in claim 1,2 or any of claims 8 to 24, and/or incorporating yarns produced by the method as claimed in any of the claim 1 or any of claims 3 to 7, or any of claims 10 to 24.

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27. A garment, article of apparel or the like clothing system, characterised by incorporating totally, predominantly or at least partially fabrics as claimed in claim 26.

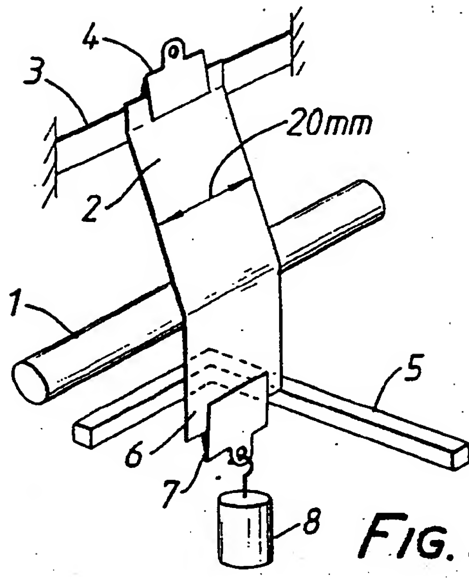

FIG. 1.

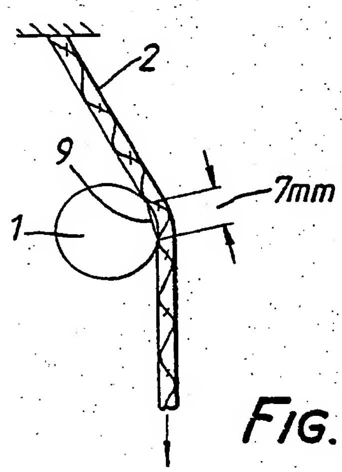

FIG. 2.

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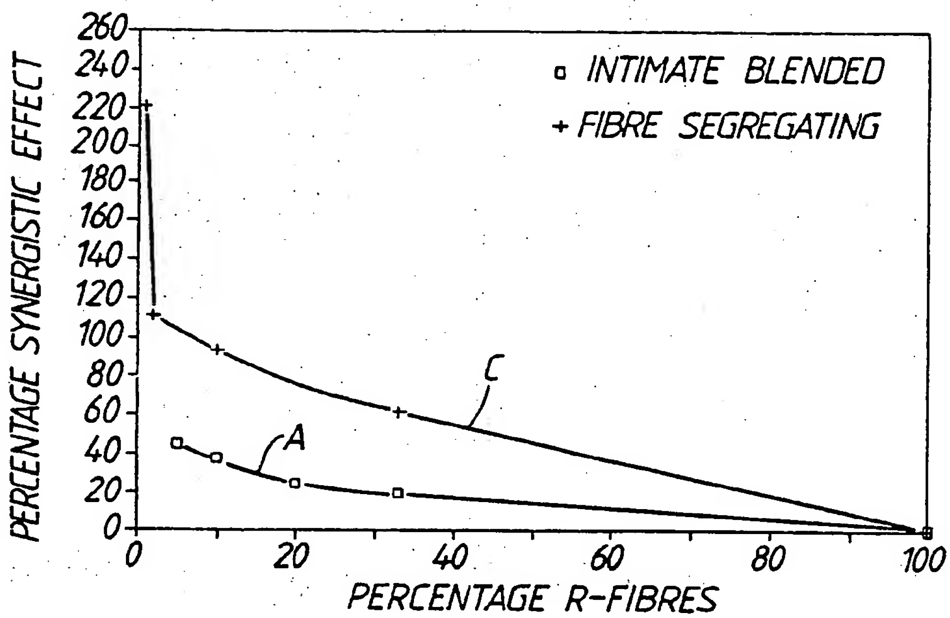
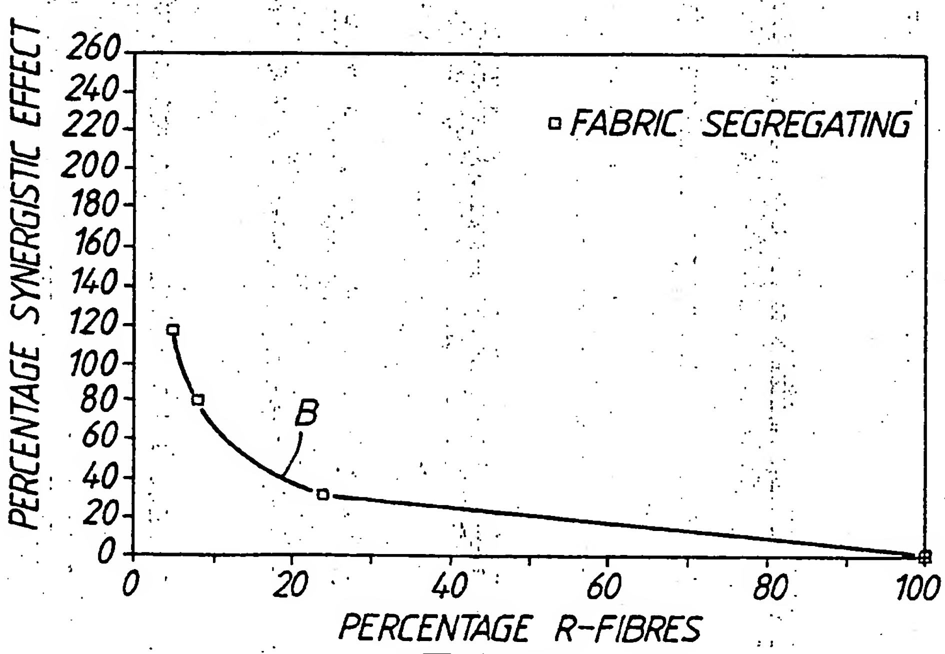


PERCENTAGE SYNERGISTIC EFFECT
260
240
220
200
180
160
140
120
100
80
60
40
20
0
INTIMATE BLENDED
+ FIBRE SEGREGATING
C
A
0
20
40
60
80
100
PERCENTAGE R-FIBRES

FIG. 3.



PERCENTAGE SYNERGISTIC EFFECT
260
240
220
200
180
160
140
120
100
80
60
40
20
0
FABRIC SEGREGATING
B
0
20
40
60
80
100
PERCENTAGE R-FIBRES

FIG. 4.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 86/00476

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: D 02 G 3/04; D 02 G 3/44; D 03 D 15/12

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	D 02 G D 03 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 3763644 (W.J. JACKSON) 9 October 1973 see column 2, lines 16-37; claims 1,7	1
X	see column 8, lines 1-7	2
A	see column 5, lines 59-60 --	26,27
A	FR, A, 2027221 (UNIROYAL INC.) 19 May 1972 see page 3, lines 26-33 --	5,25
A	US, A, 4198494 (W.G. BURCKEL) 15 April 1980 (cited in the application) ----------	

* Special categories of cited documents: [10]

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
7th October 1986	07 NOV 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 86/00476 (SA 14111)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/10/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 3763644	09/10/73	None		
FR-A- 2027221	25/09/70	NL-A-	6918986	30/06/70
		DE-A-	1961976	16/07/70
		US-A-	3572397	23/03/71
		GB-A-	1294867	01/11/72
		BE-A-	743667	24/06/70
US-A- 4198494	15/04/80	NL-A-	7511513	01/04/76
		FR-A,B	2286218	23/04/76
		BE-A-	833935	29/03/76
		DE-A,C	2543616	22/04/76
		LU-A-	73471	13/08/76
		AU-A-	8516375	31/03/77
		GB-A-	1486997	28/09/77
		AT-B-	347562	10/01/79
		CA-A-	1039939	10/10/78
		JP-A-	51060736	26/05/76
		AU-B-	498837	29/03/79
		SE-A-	7510882	31/03/76
		SE-B-	417527	23/03/81

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